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A COMPARATIVE ANALYSIS OF HARTREE-FOCK
AND KOHN-SHAM ORBITAL ENERGIES

by

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A COMPARATIVE ANALYSIS OF HARTREE-FOCK AND KOHN-SHAM ORBITAL ENERGIES

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Abstract. Hartree-Fock and Kohn-Sham orbital energies, the latter computed with several different exchange/correlation functionals, are compared and analyzed for twelve molecules. The Kohn-Sham energies differ significantly from experimental ionization energies, but by amounts that are, for a given molecule and exchange/correlation functional, roughly the same for all of the valence orbitals. With the exchange/correlation functionals used, the energy of the highest occupied Kohn-Sham orbital does not approximate the corresponding ionization potential any better than do the other orbital energies.

Key words: Hartree-Fock orbital energies, Kohn-Sham orbital energies, ionization potentials.

Introduction

The Hartree-Fock method and the Kohn-Sham version of density functional theory have in common the feature that they both involve the iterative solution of a set of one-particle eigenequations [1-3]. The resulting eigenfunctions $\{\phi_i\}$ and their associated eigenvalues $\{\epsilon_i\}$ are generally designated as atomic or molecular orbitals (depending upon the system in question) and their corresponding orbital energies.

In Hartree-Fock theory, the physical interpretation of these orbital energies is based upon the approximation,

$$I_i = E_{\text{HF}}(N-1, i) - E_{\text{HF}}(N) \quad (1)$$

in which I_i is the ionization potential of an electron in orbital ϕ_i , $E_{\text{HF}}(N)$ is the energy of the N -electron parent system and $E_{\text{HF}}(N-1, i)$ is the energy after removal of an electron from ϕ_i , leaving the geometry and other orbitals unchanged. Since it can easily be shown that [4, 5],

$$E_{\text{HF}}(N-1, i) - E_{\text{HF}}(N) = -\epsilon_{\text{HF}, i} \quad (2)$$

then it can be inferred that $-\epsilon_{\text{HF}, i} = I_i$, i.e. the magnitudes of the Hartree-Fock orbital energies, $\{|\epsilon_{\text{HF}, i}|\}$, can be viewed as approximately equal to the ionization potentials, $\{I_i\}$, of the respective electrons [4, 5]. Some justification for eq. (1) comes from Koopmans' theorem [4, 6], which assures that the wave function obtained by simply removing an electron from ϕ_i is stable with respect to further variation in ϕ_i . However eq. (1) still neglects the fact that loss of an electron produces a spatial rearrangement of the charge in the remaining orbitals, stabilizing the ion; this factor in itself would cause $|\epsilon_{\text{HF}, i}|$ to overestimate I_i . On the other hand, electronic correlation, which is omitted in Hartree-Fock

theory, is expected to lower $E_{\text{HF}}(N)$ more than $E_{\text{HF}}(N-1,i)$; this alone would make $|\epsilon_{\text{HF},i}|$ underestimate I_i . In Hartree-Fock calculations, therefore, the effects of these two sources of error should partially cancel [2, 5].

There has been considerable discussion of the physical interpretation (if any) to be given the orbital energies $\{\epsilon_{\text{KS},i}\}$ in Kohn-Sham theory [2, 3, 7-11], in which Koopmans' theorem is not applicable. The general conclusion has been that the energy of the highest occupied orbital (hoo) in exact Kohn-Sham theory should be equal in magnitude to the first ionization potential,

$$-\epsilon_{\text{KS,hoo}} = I_{\text{min}} \quad (3)$$

but that no specific physical meaning can be assigned to the other orbital energies [2, 3, 7-12]. Eq. (3) requires that the Kohn-Sham effective potential approach zero asymptotically, a point that has recently been discussed [12-14].

Our present objective is to provide and to analyze quantitative data relevant to these points. Our primary focus will be on approximate Kohn-Sham orbital energies, obtained using several different exchange/correlation functionals, but Hartree-Fock values are also included, for completeness and for perspective. These computed results will be compared to experimentally-determined electronic ionization potentials for a group of twelve molecules.

Procedures

Hartree-Fock and Kohn-Sham geometry optimizations were carried out with Gaussian 94 [15] for eleven polyatomic molecules. Four different basis sets were used for the Hartree-Fock calculations: STO-3G, 3-21G, 6-31G* and 6-31+G**. The Kohn-Sham results were obtained with several combinations of exchange and correlation functionals, including the Becke (B) [16], the Becke three-parameter hybrid (B3) [17], the Perdew 86 (P86) [18],

the Lee-Yang-Parr (LYP) [19] and the Perdew-Wang 91 (PW91) [20]. The basis set for most of the Kohn-Sham work was the 6-31+G**; however the B3P86 calculations were also carried out at the 6-311++G(3df, 3pd) level, to assess the effect of a rather large basis set. The computed orbital energies are compared to experimentally-determined vertical ionization potentials obtained through photoelectron spectroscopy; the latter data are taken primarily from the compilation by Duffy and Chong [21].

Results

Table 1 summarizes our results for the eleven molecules treated in the present study plus one (N₂O) for which the calculations were carried out earlier [22]. For each molecule are given the differences between the experimental ionization potentials [21] and the magnitudes of the orbital energies as computed by nine different Hartree-Fock and Kohn-Sham procedures. The highest occupied orbitals are listed first, followed by several valence orbitals in order of increasing I_i . The calculated total molecular energies decrease from left to right across the table, the one exception being that $E(\text{B3PW91}) < E(\text{BLYP})$ for cyclopropene.

Discussion

For the twelve molecules in Table 1, the magnitudes of the Hartree-Fock orbital energies are overall closer to the corresponding ionization potentials than are the approximate Kohn-Sham energies. The Hartree-Fock (except for the STO-3G) usually overestimate and the Kohn-Sham underestimate the experimental values. Thus in general,

$$-\epsilon_{\text{KS},i} < I_i < -\epsilon_{\text{HF},i} \quad (4)$$

as was found earlier for atoms [8, 11] and for N_2O [22].

The Hartree-Fock 6-31G* and 6-31+G** results are quite similar, as are also, for the most part, the 3-21G. These three basis sets are all relatively effective in predicting the ionization potential for the highest occupied orbital; the average absolute error is 0.7 ev, and would be 0.5 ev if not for the OF_2 molecule. (The 3-21G basis set usually gives the best agreement.) The predictions tend to be considerably poorer for the lower orbitals, but no consistent pattern is apparent. (The STO-3G results are particularly erratic.) For a given molecule and basis set, the quantities $(-\epsilon_{HF,i} - I_i)$ cover rather large ranges, typically 2 - 3 ev.

In contrast to the Hartree-Fock, the Kohn-Sham results do show certain patterns:

- (1) The Kohn-Sham orbital energies differ from the ionization potentials by at least 2 ev and often much more. This apparently reflects a need to more effectively remove electronic self-interaction [8, 11]. However the quantities $(-\epsilon_{KS,i} - I_i)$, for a given molecule and exchange/correlation combination, show a notable uniformity, usually being within a range of 0.3 - 0.7 ev. At these levels of approximation, the energy of the highest occupied orbital does not provide a better estimate of the corresponding ionization potential than do the other orbital energies. This is true even when a large basis set, 6-311++G(3df,3pd), is used.
- (2) The closest agreement between $-\epsilon_{KS,i}$ and I_i is found for the B3P86 calculations, the magnitude of the average difference $(-\epsilon_{KS,i} - I_i)_{ave}$ generally being less than 3.0 ev. This is observed for both the B3P86/6-31+G** and the B3P86/6-311++G(3df,3pd) calculations; thus the considerable increase in the basis set has little effect.
- (3) Very similar results are obtained with both the B3PW91 and the B3LYP exchange/correlation combinations; their average differences, $(-\epsilon_{KS,i} - I_i)_{ave}$, are consistently about 0.6 ev greater in magnitude than the B3P86 for the same molecule. Finally, the BLYP results are worse by approximately an additional 1.7 ev,

presumably because the hybrid (B3) procedures explicitly include a Hartree-Fock exchange contribution [15, 17].

In Figure 1 is shown the remarkably parallel behavior of the average differences obtained with the various functional combinations. This is particularly notable in view of the uncertainties associated with some of the experimental ionization potentials. Figure 1 suggests that the several computed magnitudes of $(-\epsilon_{\text{KS},i} - I_i)_{\text{ave}}$ for each molecule may be related to some property of that molecule. Recent work has drawn attention to the quantity $0.5(I_{\text{min}} - A)$ in relation to the asymptotic behavior of the Kohn-Sham effective potential [13, 14], where A is the molecule's electron affinity. However we have thus far found no similarity between the variations of $0.5(I_{\text{min}} - A)$ and the several $(-\epsilon_{\text{KS},i} - I_i)_{\text{ave}}$.

Finally, in view of the interest in the quantity $0.5(I_{\text{min}} - A)$ as well as in the difference between the Kohn-Sham highest-occupied and lowest-unoccupied orbital energies, $\epsilon_{\text{KS},\text{hoo}}$ and $\epsilon_{\text{KS},\text{lvo}}$ [9, 11], Figure 2 shows the variation of $0.5(\epsilon_{\text{KS},\text{lvo}} - \epsilon_{\text{KS},\text{hoo}})$ among the different molecules, for each exchange/correlation combination. The most striking feature is the near-uniformity of the results, other than the BLYP.

Conclusions

The important points coming out of this work are the following:

- (1) The magnitudes of the Kohn-Sham orbital energies differ significantly from experimental ionization potentials. However the amount by which they differ, for a given molecule and exchange/correlation combination, is usually roughly the same for all of the valence orbitals.
- (2) With the present exchange/correlation functionals, the energy of the highest occupied Kohn-Sham orbital does not provide a better estimate of the corresponding ionization potential than do the other valence orbital energies.

- (3) The average differences between the magnitudes of the Kohn-Sham orbital energies and the experimental ionization potentials vary from molecule to molecule.

However they are always least for the B3P86 calculations, about 0.6 eV greater for the B3PW91 and B3LYP, and approximately an additional 1.7 eV larger for the BLYP.

- (4) These remarkable consistencies suggest that the differences may be related to some property of the molecule.

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Table 1. Differences between computed orbital energies and experimental ionization potentials, in eV.^a

Molecule	Molecular orbital, ϕ_i	$-\epsilon_{\text{HF},i} - I_i$				$-\epsilon_{\text{KS},i} - I_i$				
		STO-3G	3-21G	6-31G*	6-31+G**	B3PW91 ^b	BLYP ^b	B3LYP ^b	B3P86 ^b	B3P86 ^c
N ₂	3 σ_g	-1.17	1.17	1.59	1.71	-3.70	-5.37	-3.65	-3.12	-3.09
	1 π_u	-2.05	-0.12	-0.11	0.04	-4.07	-5.61	-4.11	-3.49	-3.41
	2 σ_u	1.02	1.81	2.17	2.30	-3.41	-5.23	-3.43	-2.83	-2.96
H ₂ O	1b ₁	-1.94	0.37	0.94	1.25	-3.93	-5.53	-3.88	-3.36	-3.26
	3a ₁	-2.23	-0.32	0.79	1.07	-4.03	-5.62	-4.01	-3.46	-3.32
	1b ₂	-2.35	0.14	0.93	1.43	-3.75	-5.47	-3.76	-3.19	-3.23
HCN	1 π	-1.78	-0.21	-0.28	-0.10	-3.67	-5.04	-3.70	-3.10	-3.02
	5 σ	-0.73	1.29	1.46	1.65	-3.47	-5.06	-3.45	-2.90	-2.90
	4 σ	0.70	2.16	2.32	2.46	-2.90	-4.64	-2.90	-2.33	-2.35
CO ₂	1 π_g	-3.2	0.5	1.0	1.2	-3.2	-4.7	-3.2	-2.6	-2.6
	1 π_u	-0.7	2.1	2.0	2.2	-3.2	-5.1	-3.3	-2.7	-2.6
	2 σ_u	-2.1	1.6	2.1	2.3	-3.5	-5.4	-3.5	-3.0	-2.9
	2 σ_g	-0.9	1.6	2.2	2.4	-3.7	-5.6	-3.7	-3.1	-3.2
N ₂ O	2 π	-3.20	0.04	0.49	0.65	-3.24	-4.59	-3.25	-2.66	-2.67
	7 σ	-0.45	2.37	2.53	2.67	-3.08	-4.83	-3.05	-2.50	-2.57
	1 π	-0.22	2.35	2.79	2.92	-2.58	-4.64	-2.67	-2.00	-1.89
	6 σ	-0.28	1.47	2.24	2.40	-3.31	-5.19	-3.36	-2.73	-2.76
OF ₂	2b ₁	-2.44	2.33	1.83	2.16	-3.69	-5.28	-3.52	-3.12	-3.23
	6a ₁	-3.20	0.92	1.41	1.74	-3.68	-5.53	-3.65	-3.10	-3.12
	4b ₂	-2.53	1.50	1.96	2.31	-3.68	-5.48	-3.63	-3.09	-3.13
	1a ₂	-1.48	2.66	3.08	3.40	-3.51	-5.54	-3.49	-2.92	-2.91
	1b ₁	-1.06	2.08	3.51	3.86	-3.34	-5.84	-3.39	-2.73	-2.62
	5a ₁	-1.87	1.58	2.73	3.05	-3.43	-5.50	-3.51	-2.83	-2.77
	3b ₂	-2.73	0.79	1.74	2.06	-3.50	-5.45	-3.64	-2.90	-2.85

(continued)

Table 1. Differences between computed orbital energies and experimental ionization potentials, in eV (continued).^a

Molecule	Molecular orbital, ϕ_i	$-\epsilon_{HF,i} - I_i$					$-\epsilon_{KS,i} - I_i$			
		STO-3G	3-21G	6-31G*	6-31+G**	B3PW91b	BLYPb	B3LYPb	B3P86b	B3P86c
FCN	2π	-2.22	0.21	0.02	0.24	-3.63	-5.01	-3.63	-3.06	-3.06
	7σ	-0.84	1.47	1.50	1.72	-3.36	-4.91	-3.34	-2.79	-2.89
	1π	-1.6	2.0	2.7	3.0	-3.6	-5.7	-3.6	-3.0	-2.8
	6σ	-2.4	1.2	2.5	2.8	-3.5	-5.6	-3.6	-2.9	-2.8
C_2H_2	$1\pi_u$	-1.62	-0.27	-0.48	-0.25	-3.37	-4.60	-3.41	-2.82	-2.68
	$3\sigma_g$	0.0	1.8	1.6	1.9	-3.1	-4.6	-3.0	-2.5	-2.4
	$2\sigma_u$	0.5	1.9	2.0	2.2	-3.0	-4.7	-3.0	-2.5	-2.5
	$2\sigma_g$	2.8	4.7	4.4	4.7	-2.8	-5.2	-2.9	-2.3	-2.2
$H_2C=O$	$2b_3$	-1.3	0.9	0.9	1.1	-3.3	-4.7	-3.2	-2.7	-2.7
	$1b_1$	-2.4	-0.2	0.2	0.4	-3.3	-4.7	-3.3	-2.7	-2.6
	$5a_1$	-1.3	1.2	1.7	1.8	-3.5	-5.3	-3.5	-3.0	-2.9
	$1b_2$	0.2	2.0	2.0	2.1	-3.2	-5.0	-3.2	-2.7	-2.6
	$4a_1$	0.6	2.3	2.2	2.4	-3.8	-5.7	-3.8	-3.2	-3.3
$H_2C=C=O$	$2b_1$	-2.2	0.0	0.0	0.1	-2.9	-4.0	-2.9	-2.3	-2.3
	$2b_2$	-1.7	0.8	1.1	1.3	-2.9	-4.3	-2.9	-2.3	-2.3
	$1b_1$	0.4	2.6	2.6	2.8	-2.5	-4.3	-2.5	-1.9	-1.8
	$1b_2$	-0.5	1.7	1.6	1.8	-2.8	-4.5	-2.9	-2.2	-2.2
	$7a_1$	-0.7	1.6	1.6	1.8	-3.3	-5.0	-3.3	-2.7	-2.7
	$6a_1$	0.0	2.0	2.4	2.6	-3.2	-5.0	-3.2	-2.6	-2.6

(continued)

Table 1. Differences between computed orbital energies and experimental ionization potentials, in eV (continued).^a

Molecule	Molecular orbital, ϕ_i	$-\epsilon_{HF,i} - I_i$				$-\epsilon_{KS,i} - I_i$			
		STO-3G	3-21G	6-31G*	6-31+G**	B3PW91 ^b	BLYP ^b	B3LYP ^b	B3P86 ^b B3P86 ^c
$\begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{HC}=\text{CH} \end{array}$	2b ₂	-1.42	-0.01	-0.18	-0.08	-2.86	-3.94	-2.87	-2.31 -2.24
	3b ₁	-0.62	0.49	0.43	0.54	-2.70	-3.98	-2.75	-2.14 -2.09
	6a ₁	-0.4	0.8	0.7	0.8	-3.1	-4.5	-3.1	-2.6 -2.5
	1b ₂	0.25	1.36	1.09	1.21	-3.15	-4.73	-3.20	-2.59 -2.50
	5a ₁	0.66	2.04	1.86	1.96	-2.87	-4.51	-2.88	-2.30 -2.24
	2b ₁	1.3	2.5	2.5	2.6	-2.8	-4.6	-2.8	-2.2 -2.2
	4a ₁	1.7	3.0	2.8	2.9	-3.2	-5.1	-3.2	-2.6 -2.6
	3b ₁	-0.87	0.18	0.38	0.45	-2.89	-4.15	-2.92	-2.32 -2.36
$\begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{N}=\text{N} \end{array}$	2b ₂	-1.76	0.47	0.13	0.24	-3.27	-4.52	-3.25	-2.71 -2.69
	6a ₁	-0.71	1.45	1.77	1.89	-3.06	-4.69	-3.05	-2.48 -2.45
	5a ₁	-0.2	1.4	1.9	1.9	-2.9	-4.6	-2.9	-2.3 -2.3
	1b ₂	0.1	1.5	1.5	1.5	-3.1	-4.9	-3.2	-2.6 -2.5
	2b ₁	1.7	2.6	2.7	2.8	-3.4	-5.4	-3.5	-2.8 -2.9
	4a ₁	2.3	4.0	3.8	3.9	-2.7	-4.8	-2.7	-2.1 -2.1
	3b ₁	-0.87	0.18	0.38	0.45	-2.89	-4.15	-2.92	-2.32 -2.36
	2b ₂	-1.76	0.47	0.13	0.24	-3.27	-4.52	-3.25	-2.71 -2.69

^aExperimental ionization potentials are from reference 21, except those for CO₂, which are from P. K. Ghosh, *Introduction to Photoelectron Spectroscopy*, Wiley-Interscience, New York, 1983, Table 5.3.

^bBasis set = 6-31+G**.

^cBasis set = 6-311++G(3df,3pd).

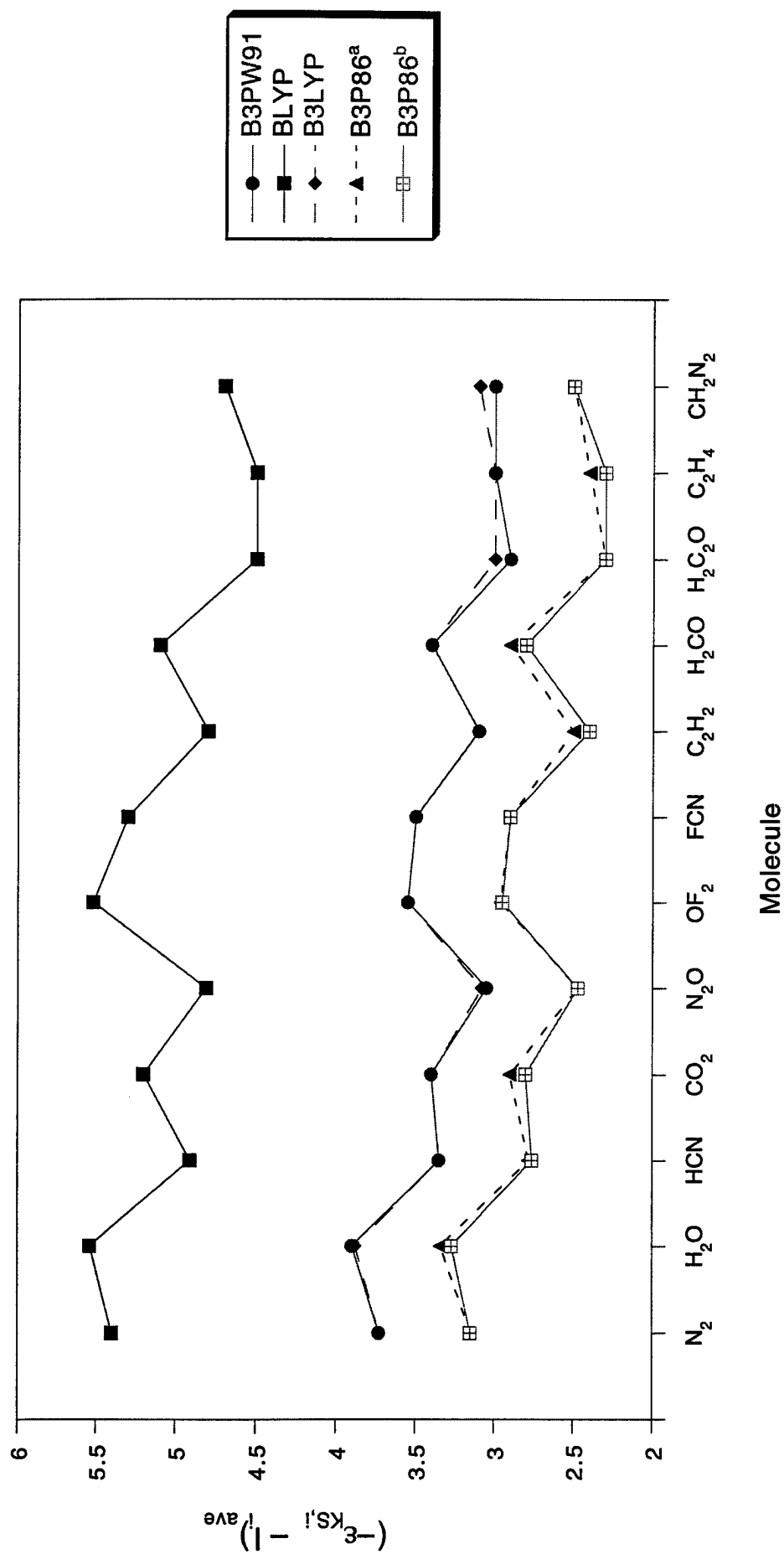


Figure 1. Dependence of $(-\epsilon_{\text{KS},i} - I)_{\text{ave}}$, in ev, upon computational method, for molecules included in this study. The superscripts a and b denote the two B3P86 basis sets, 6-31+G** and 6-311++G(3df, 3pd), respectively.

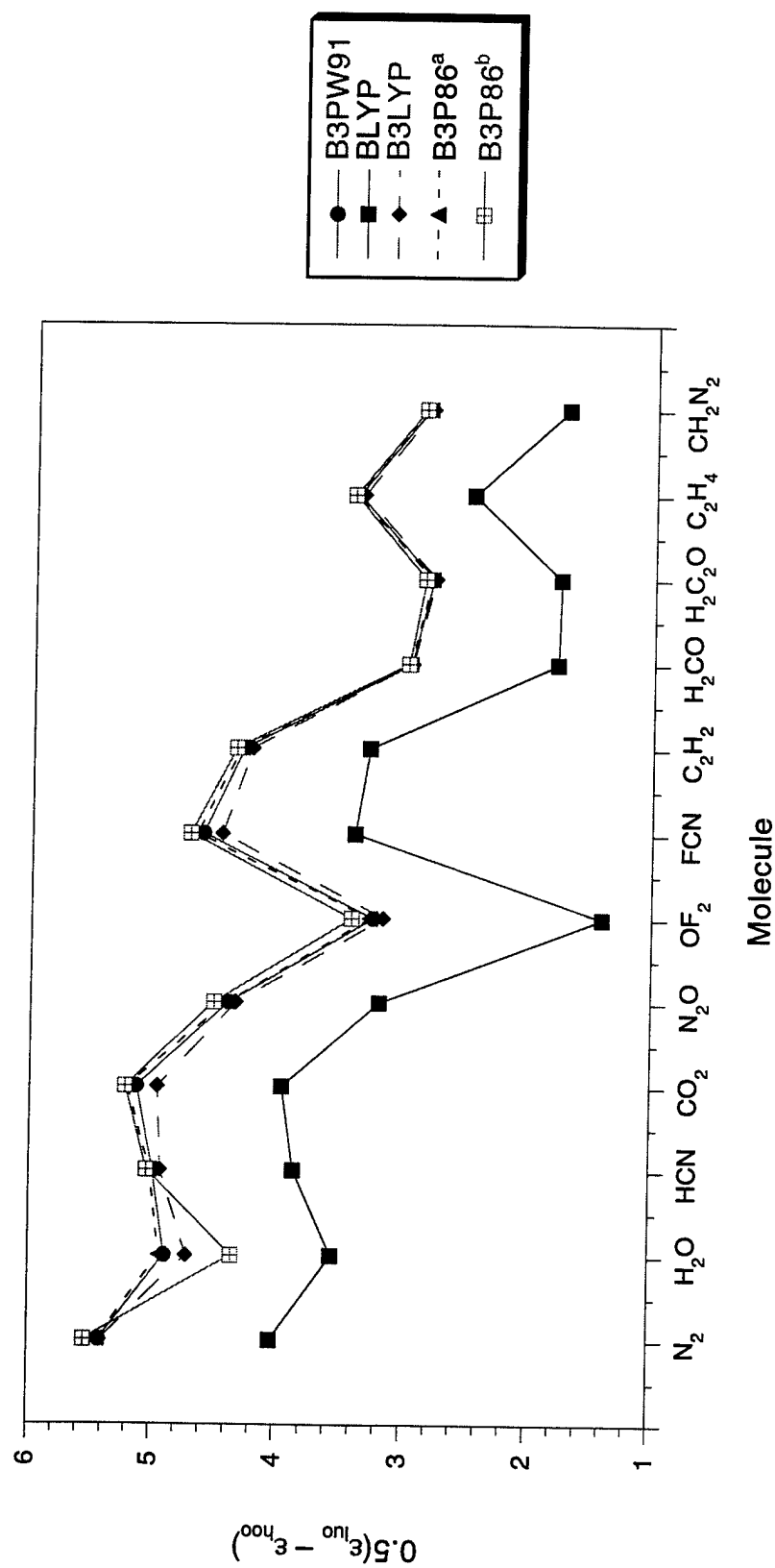


Figure 2. Dependence of $0.5(\epsilon_{\text{luo}} - \epsilon_{\text{hoo}})$, in ev, upon computational method, for molecules included in this study. The superscripts a and b denote the two B3P86 basis sets, 6-311+G** and 6-311++G(3df, 3pd), respectively.